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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Polyurethane Dispersions

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#### Polyurethane dispersions

- 5 Aqueous polyurethane dispersions are described in EP 98 752. These polyurethane dispersions are prepared by first reacting a diol containing ionic groups, a polyol-polyether or polyol-polyester and an excess of a diisocyanate to form a prepolymer. In the second stage, this  
10 prepolymer, which contains free isocyanate groups, is then reacted with a hydroxy-alkyl (meth)acrylate. This gives a second prepolymer which contains vinyl groups, and this prepolymer is then finally polymerized in an aqueous dispersion using initiators which form free  
15 radicals. In the polyurethanes described here, the vinyl group is achieved exclusively by incorporation of hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl (meth)acrylates. Incorporation of other monomers for the formation of vinyl groups is not mentioned therein.
- 20 The present invention relates to polyurethane dispersions which are prepared by polymerization, initiated by free radicals, of polyurethane macromonomers containing carboxyl, phosphonic acid or sulfonic acid groups, terminal vinyl groups and optionally urethane, thiourethane  
25 and/or urea groups, the terminal vinyl groups not being derived from hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl (meth)acrylates. These polyurethane macromonomers can be prepared by polyaddition of polyhydroxy compounds from the group comprising polyhydroxy-polyethers, polyhydroxy-polyesters  
30 and polyhydroxy-polycarbonates, and furthermore polyhydroxycarboxylic acids, polyhydroxyphosphonic acids and polyhydroxysulfonic acids, and polyisocyanates.

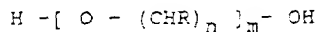
The mixing ratios here are selected so that the polyisocyanate is in excess, so that the prepolymer

formed contains free isocyanate groups in addition to the carboxyl, phosphonic acid and sulfonic acid groups. In a preferred procedure, it is also possible first to employ the polyisocyanate in a substoichiometric amount, in order  
 5 in this way to obtain a prepolymer containing free hydroxyl groups. In an additional step, this prepolymer is then reacted with further polyisocyanate, in order in this way likewise to obtain a prepolymer containing free isocyanate groups.

10 These prepolymers are then further reacted with a monomer containing, in addition to a vinyl group, a group which reacts with isocyanate groups, such as, for example, the hydroxyl, amino or mercapto group. Examples of these are products of the reaction of monoepoxides and  $\alpha,\beta$ -  
 15 unsaturated carboxylic acids, such as, for example, products of the reaction of glycidyl versatate and (meth)acrylic acid or 2-ethylhexyl glycidyl ether and (meth)acrylic acid, products of the reaction of  $\alpha,\beta$ -  
 20 unsaturated glycidyl esters or ethers with monocarboxylic acids, for example products of the reaction of glycidyl methacrylate and stearic acid or linseed oil fatty acid and furthermore (meth)acrylates containing amino groups, such as, for example, t-butylaminoethyl methacrylate.

These monomers can be used by themselves, but it is also  
 25 possible for these monomers to be employed as a mixture with primary or secondary amines, alcohols or thioalcohols. A macromonomer which contains terminal vinyl groups is obtained in this manner. This macromonomer is then polymerized in the last stage via  
 30 the vinyl groups using initiators which form free radicals.

Possible polyhydroxy-polyethers are compounds of the formula



in which

R is hydrogen or a lower alkyl radical, optionally with various substituents,

n is a number from 2 to 6 and

5 m is a number from 10 to 120.

Examples are poly(oxytetramethylene) glycols, poly(oxyethylene) glycols and poly(oxypropylene) glycols.

The preferred polyhydroxy-polyethers are poly(oxypropylene) glycols having a molecular weight in  
10 the range from 400 to 5000.

The polyhydroxy-polyesters are prepared by esterification of organic polycarboxylic acids or their anhydrides with organic polyols. The polycarboxylic acids and the polyols can be aliphatic or aromatic polycarboxylic acids and  
15 polyols.

The polyols used for the preparation include alkylene glycols, such as ethylene glycol, butylene glycol, hexane-1,6-diol, neopentylglycol and other glycols, such as, for example, dimethylolcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane and trishydroxyalkylalkanes, such as, for example, trimethylolpropane, and  
20 tetrakis(hydroxyalkyl)alkanes, such as, for example, pentaerythritol.

The acid component of the polyester primarily consists of  
25 low molecular weight polycarboxylic acids or their anhydrides having 2 to 18 carbon atoms in the molecule.

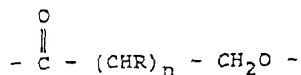
Suitable acids are, for example, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, hexachloroheptanedicarboxylic acid, alkyl- and alkenylsuccinic acid, for example n-octenylsuccinic acid and n-  
30 and iso-dodecenylsuccinic acid, tetrachlorophthalic acid,

trimellitic acid and pyromellitic acid. Instead of these acids, their anhydrides, where these exist, can also be used. Dimeric and trimeric fatty acids can also be employed as the polycarboxylic acids.

- 5 The terms polyhydroxy-polyether and polyhydroxy-polyester are also to be understood as meaning those products of this type which contain monomers having carboxyl, sulfonate or phosphonate groups.

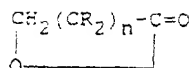
- 10 Polyhydroxy-polyesters which are derived from lactones can furthermore be used in the invention. These products are obtained, for example, by reaction of an  $\epsilon$ -caprolactone with a polyol. Such products are described in US-PS 3 169 945.

- 15 The polylactone-polyols which are obtained by this reaction are distinguished by the presence of a terminal hydroxyl group and by recurring polyester contents which are derived from the lactone. These recurring molecular contents can correspond to the formula



- 20 in which n is preferably 4 to 6 and the substituent is hydrogen, an alkyl radical, a cycloalkyl radical or an alkoxy radical, no substituent containing more than 12 carbon atoms.

- 25 The lactone used as the starting material can be any desired lactone or any desired combination of lactones, and this lactone should contain at least 6 carbon atoms in the ring, for example 6 to 8 carbon atoms, and 2 hydrogen substituents should be present on the carbon atom bonded to the oxygen group of the ring. The lactone  
30 used as the starting material can be represented by the following general formula:

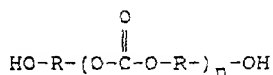


in which n and R have the meaning already given.

The lactones preferred in the invention are the  $\epsilon$ -caprolactones, in which n has the value 4. The most preferred lactone is unsubstituted  $\epsilon$ -caprolactone, in which n has the value 4 and all the R substituents are hydrogen. This lactone is particularly preferred, since it is available in large amounts and produces coatings which have excellent properties. Various other lactones can furthermore be used individually or in combination.

Examples of aliphatic polyols which are suitable for the reaction with the lactone are ethylene glycol, 1,3-propanediol, 1,4-butanediol, hexane-1,6-diol, dimethylolcyclohexane, trimethylolpropane and pentaerythritol.

Possible starting compounds are furthermore polycarbonate-polyols and polycarbonate-diols which correspond to the general formula



where R is an alkylene radical. These OH-functional polycarbonates can be prepared by reaction of polyols, such as propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, diethylene glycol, triethylene glycol, 1,4-bis-hydroxymethylcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, neopentylglycol, trimethylolpropane or pentaerythritol, with di-carbonates, such as dimethyl, diethyl or diphenyl carbonate, or phosgene. Mixtures of such polyols can likewise be employed.

The polyhydroxy-polyethers, polyhydroxy-polyesters and polyhydroxy-polycarbonates described above can be employed together. These polyhydroxy compounds can moreover also be employed together with various amounts  
5 of low molecular weight isocyanate-reactive polyols, polyamines or polymercaptans. Possible compounds of this type are, for example, ethylene glycol, butanediol, pentaerythritol, trimethylolpropane, ethylenediamine, propylenediamine and hexamethylenediamine.

- 10 Low molecular weight polyols, preferably diols, which moreover also contain an ionic group in the form of the carboxylic acid, phosphonic acid or sulfonic acid group are employed as a further unit for the preparation of the polyurethane dispersions according to the invention.
- 15 Examples of this group of monomers are  $\alpha$ -C<sub>2</sub>-C<sub>10</sub>-bis-hydroxycarboxylic acids, such as, for example, dihydroxypropionic acid, dimethylolpropionic acid, dihydroxyethylpropionic acid, dimethylolbutyric acid, dihydroxysuccinic acid and dihydroxybenzoic acid, or 3-hydroxy-2-hydroxy-
- 20 methylpropanesulfonic acid and 1,4-dihydroxybutanesulfonic acid.

These monomers can be neutralized before the reaction with a tertiary amine, such as, for example, trimethylamine, triethylamine, dimethylaniline, diethyl-

25 aniline or triphenylamine, in order to avoid reaction of the acid group with the isocyanate. If the probability of such a reaction is only slight, the acid groups can also be neutralized only after their incorporation into the polyurethane microgel. The neutralization is then carried

30 out with aqueous solutions of alkali metal hydroxides or with amines, for example with trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, aminomethylpropanol, dimethylaminomethylpropanol and

35 dimethylisopropanolamine, or with ammonia. In addition, the neutralization can also be carried out with mixtures

of amines and ammonia.

Examples of suitable polyisocyanates are trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylethylene diisocyanate, 2,3-dimethylethylenediisocyanate, 1-methyltrimethylene diisocyanate, cyclopentylene 1,3-diisocyanate, cyclohexylene 1,4-diisocyanate, cyclohexylene 1,2-diisocyanate, phenylene 1,3-diisocyanate, phenylene 1,4-diisocyanate, toluylene 2,4-diisocyanate, toluylene 2,6-diisocyanate, biphenylene 4,4'-diisocyanate, naphthylene 1,5-diisocyanate, naphthylene 1,4-diisocyanate, 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, bis-(4-isocyanatocyclohexyl)-methane, bis-(4-isocyanatocyclophenyl)methane, 4,4'-diisocyanatodiphenyl ether, 2,3-bis-(8-isocyanatooctyl)-4-octyl-5-hexylcyclohexene, tetramethylxylylene diisocyanates, trimethylhexamethylene diisocyanates, isocyanurates of the above diisocyanates or allophanates of the above diisocyanates. Mixtures of such di- or polyisocyanates can likewise be employed.

It is of particular importance for the polyurethane dispersions according to the invention that the macromonomers which lead to these dispersions contain terminal vinyl groups. The term terminal vinyl groups is intended to mean those vinyl groups which hang on the start or end of the polymer chain. Terminal vinyl groups are incorporated by reacting a prepolymer obtained by reaction of the polyols and the polyhydroxycarboxylic, polyhydroxyphosphonic or polyhydroxysulfonic acids and containing free isocyanate groups with a vinyl monomer of the abovementioned type which contains a group which is reactive toward isocyanate groups.

The macromonomers built up from these monomers can additionally also be modified by incorporating amines, alcohols and/or thioalcohols. For this modification, the



intermediate product produced in the first stage, which contains terminal isocyanate radicals, is reacted not by itself with the vinyl monomer which contains an isocyanate-reactive group, but this monomer is reacted  
5 together with amines, alcohols and/or thioalcohols. Possible reactants here are, for example, primary amines, such as propylamine, butylamine, pentylamine, 2-amino-2-methylpropanol, ethanolamine and propanolamine; secondary  
10 amines, such as diethanolamine, dibutylamine and diisopropanolamine; primary alcohols, such as methanol, ethanol, propanol, butanol, hexanol, dodecanol and stearyl alcohol; and secondary alcohols, such as isopropanol and isobutanol, and the corresponding thioalcohols.

15 The preparation of the intermediate products in the first stages is carried out by the customary methods which are known in urethane chemistry. Tertiary amines, such as, for example, triethylamine, dimethylbenzylamine and diazabicyclooctane, and dialkyltin(IV) compounds, such  
20 as, for example, dibutyltin dilaurate, dibutyltin dichloride and dimethyltin dilaurate, can be employed as catalysts here. The reaction takes place in the melt without a solvent, in the presence of a solvent or in the presence of a so-called reactive diluent. Possible  
25 solvents are those which can be removed later by distillation, for example dioxane, methyl ethyl ketone, methyl isobutyl ketone, acetone, tetrahydrofuran, toluene and xylene. These solvents can be completely or partly distilled off after the preparation of the polyurethane  
30 macromonomers or after the free radical polymerization. In addition, the reaction can also be carried out in a high-boiling water-dilutable solvent, for example in N-methylpyrrolidone, this then remaining in the dispersion. Further solvents, such as, for example,  
35 glycol ethers and esters thereof, can also be added before the dispersing process. Suitable glycol ethers are, for example, butylglycol, butyldiglycol,

- methoxypropanol, dipropylene glycol monomethyl ether or diglycol dimethyl ether. The reactive diluents are  $\alpha,\beta$ -unsaturated monomers, which are copolymerized with the macromonomers containing vinyl groups in the final stage.
- 5 Examples of such reactive diluents are  $\alpha,\beta$ -unsaturated vinyl monomers, such as alkyl acrylates, methacrylates and crotonates having 1 to 20 carbon atoms in the alkyl radical, di-, tri- and tetraacrylates, -methacrylates and -crotonates of glycols, tri- and tetrafunctional
- 10 alcohols, substituted and unsubstituted acryl- and methacrylamides, vinyl ethers,  $\alpha,\beta$ -unsaturated aldehydes and ketones, vinyl alkyl ketones having 1 to 20 carbon atoms in the alkyl radical, vinyl ethers, vinyl esters, diesters of  $\alpha,\beta$ -unsaturated dicarboxylic acids, styrene
- 15 and styrene derivatives, such as, for example,  $\alpha$ -methylstyrene.

- The intermediates obtained in this way from the first step are then reacted, without intermediate isolation, under the same conditions with the isocyanate-reactive
- 20 vinyl monomers, where amines, alcohols or thioalcohols are also suitable, as mentioned above, in addition to the isocyanate-reactive vinyl monomers. The mixing ratios are selected in each case so that all the isocyanate groups are converted into urethane, thiourethane or urea groups.

- 25 The macromonomers thus obtained are then neutralized, if the acid groups in the monomers which carry such groups have not already been employed in the neutralized form from the beginning. The neutralization is then carried out with aqueous solutions of alkali metal hydroxides or
- 30 with amines, for example with trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, aminomethylpropanol, dimethylaminomethylpropanol or dimethylisopropanolamine, or with ammonia. In addition,
- 35 the neutralization can also be carried out with mixtures of amines and ammonia.

To prepare the polyurethane dispersions according to the invention, macromonomers which contain vinyl groups are converted into an aqueous dispersion by addition of water and polymerized by methods which are known per se using  
5 initiators which form free radicals. If so-called reactive diluents are not present from the beginning, monomers of this type, as described above, can be incorporated into the polyurethane as copolymerized units during this polymerization. Carboxyl-, hydroxyl-, amino-,  
10 ether- and mercapto-functional  $\alpha,\beta$ -unsaturated vinyl monomers can also furthermore additionally be added immediately before or during the free radical polymerization. Examples of these are hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate,  
15 meth(acrylic) acid, crotonic acid, glycidyl (meth)acrylate, t-butylaminoethyl methacrylate and dimethylaminoethyl methacrylate. The content of copolymerized vinyl monomers is 0 to 95% by weight, preferably 5 to 70% by weight, based on the solid of the  
20 polyurethane dispersion. The ratio of flexible and rigid segments in the polyurethane macromonomers is 0.30 to 6, particularly preferably 0.8 to 3. Possible initiators for the polymerization are the known initiators which form free radicals, such as ammonium peroxydisulfate,  
25 potassium peroxide-sulfate, sodium peroxide-sulfate, hydrogen peroxide, organic peroxides, such as, for example, cumene hydroperoxide, t-butyl hydroperoxide, di-tert-butyl peroxide and dioctyl peroxide, tert-butyl perpivalate, tert-butyl perisononanoate, tert-butyl  
30 perethylhexanoate, tert-butyl perneodecanoate, di-2-ethylhexyl peroxydicarbonate, diisotridecyl peroxydicarbonate and azo compounds, such as, for example, azo-bis(isobutyronitrile) and azo-bis(4-cyanovaleric acid), or the customary redox systems, for  
35 example sodium sulfite, sodium dithionite and ascorbic acid and organic peroxides or hydrogen peroxide. Regulators (mercaptans), emulsifiers, protective colloids and other customary auxiliaries can moreover also be

added.

If the preparation of the macromonomer has been carried out in a solvent which can be removed by distillation and either forms an azeotrope with water or can be  
5 fractionated out of the aqueous phase, for example in acetone, dioxane, methyl ethyl ketone, methyl isobutyl ketone, tetrahydrofuran, toluene or xylene, this solvent is removed from the dispersion by distillation. Aqueous polyurethane dispersions are obtained in all cases.

10 The acid numbers of these polyurethanes are in the range from 5 to 80, particularly preferably in the range from 10 to 40 units.

Further details on the preparation of the macromonomers and polymerization thereof to give the polyurethane  
15 dispersions according to the invention can be seen from the following general process descriptions. These process conditions are preferred embodiments.

#### 1. Solvent-free

##### a. without an auxiliary solvent

20 At temperatures of 100 to 150°C, particularly preferably 120 to 135°C, the polyhydroxy acid and if appropriate low molecular weight polyols are dissolved in a polyol having an average molecular weight of 400 to 5000 and reacted with a polyisocyanate or polyisocyanate mixtures to give  
25 a product which has OH end groups and has an average molecular weight (Mn) of 500 to 12,000, particularly preferably 600 to 8000. After the product has been cooled to a temperature of 30 to 100°C, particularly preferably 50 to 80°C, a comonomer which is not isocyanate-reactive  
30 is added. A resin containing terminal NCO groups is built up at this temperature by further addition of polyisocyanate, and the product is then reacted with a monofunctional, NCO-reactive vinyl compound to give a polyurethane macromonomer having an average molecular

weight of 700 to 24,000, particularly preferably 800 to 16,000. This resulting resin solution is neutralized with amines or other bases and dispersed in water. Other vinyl comonomers can also be added to the resulting dispersion before or during the free radical polymerization which is still to be carried out. The free vinyl compounds are then polymerized in the aqueous dispersion using initiators which form free radicals, at a temperature of 0 to 95°C, particularly preferably 40 to 95°C, and at a temperature of 30 to 70°C if redox systems are used. A solvent-free polyurethane dispersion is formed here.

**b. with an auxiliary solvent**

In contrast to process 1.a., in this case all the polyol components are dissolved in a solvent which can be fractionated out of the aqueous phase or forms an azeotrope with water and are reacted directly with polyisocyanate or polyisocyanate mixtures to give the product which contains terminal NCO groups. The solvent content is 1 to 80% by weight, particularly preferably between 10 and 50% by weight, based on the solid of the polyurethane macromonomer. The temperature for this step is between 30 and 100°C, particularly preferably between 50 and 80°C. After the reaction with a monofunctional, isocyanate-reactive vinyl compound to give a polyurethane macromonomer having a molecular weight of 500 to 30000, particularly preferably 700 to 20000, the product is neutralized with amines or other bases and dispersed in water. The auxiliary solvent is then distilled off from the aqueous phase, if necessary under a slight vacuum. Vinyl comonomers can also be added to this solvent-free dispersion before or during the free radical polymerization which is still to be carried out. Polymerization is then carried out with initiators which form free radicals, at a temperature of between 0 and 95°C, particularly preferably between 40 and 95°C, and at a temperature of 30 to 70°C if redox systems are used, to give a solvent-free polyurethane dispersion.

## 2. Containing solvent

If a non-distillable auxiliary solvent, such as, for example, N-methylpyrrolidone, is used, the procedure is exactly as in process 1.b., but the distillation after  
5 the dispersing operation is omitted. If appropriate vinyl monomers can here be added before or during the polymerization. The polymerization is carried out as in process 1.b. The solvent content is in the range from 0.1 to 30% by weight, particularly preferably 1 to 15% by  
10 weight, based on the total binder dispersion.

Because of their chemical build-up, the polyurethane dispersions according to the invention are suitable for diverse uses, for example for the preparation of coating systems, inter alia for coating wood, as binders for  
15 water-dilutable adhesives or as resins for printing inks.

They can be combined with and are in general compatible with other aqueous dispersions and solutions of plastics, for example acrylic and/or methacrylic polymers, polyurethane, polyurea resins, polyester resins and epoxy  
20 resins, thermoplastics based on polyvinyl acetate, -vinyl chloride, -vinyl ether, -chloroprene and -acrylonitrile and ethylene/butadiene/styrene copolymers. They can also be combined with substances which have a thickening action and are based on polyacrylates or polyurethanes  
25 containing carboxyl groups, hydroxyethylcellulose, polyvinyl alcohols and inorganic thixotropic agents, such as bentonite, sodium/magnesium silicates and sodium/magnesium/fluorine/lithium silicates.

The polyurethane dispersions according to the invention  
30 can be applied to the most diverse substrates, for example ceramic, wood, glass, concrete and preferably plastics, such as polycarbonate, polystyrene, polyvinyl chloride, polyester, poly(meth)acrylates, acrylonitrile/butadiene/styrene polymers and the like, and preferably  
35 to metal, such as iron, copper, aluminum, steel, brass,

bronze, tin, zinc, titanium, magnesium and the like. They adhere to the various substrates without adhesion-promoting primers or intermediate layers.

5 The polyurethane dispersions according to the invention are suitable, for example, for the production of corrosion-preventing coatings and/or intermediate coatings for the most diverse fields of use, in particular for the production of metallic and solid base paints in multi-coat build-ups of paint for the fields of painting of  
10 automobiles and plastics, and for producing primer paints for the field of painting of plastics.

Because of the short flush-off times of the base paints based on the polyurethane dispersions according to the invention, the pigmented coat of base paint can be over-  
15 varnished with a clear varnish without a stoving step (wet-in-wet process) and the coatings can then be stoved together or subjected to forced drying. Base paints prepared with the polyurethane dispersions according to the invention give paint films of the same quality  
20 largely independently of the stoving or drying temperature, so that they can be employed both as a repair paint for motor vehicles and as a stoving paint for series painting of motor vehicles. In both cases, paint films having a good adhesion to the original coating and a good  
25 resistance to condensation water result. The brilliance of the paint coating after a condensation water test is furthermore not noticeably impaired.

The crosslinking agents customary in the paint industry, such as, for example, water-soluble or -emulsifiable  
30 melamine or benzoguanamine resins, polyisocyanates or prepolymers having terminal isocyanate groups, water-soluble or -dispersible polyaziridines and blocked polyisocyanates, can be added during formulation of water-dilutable paints using the polyurethane dispersions  
35 according to the invention. The aqueous coating systems

can contain all the pigments and dyestuffs, which can be of an inorganic or organic nature, which are known and are customary in paint technology, as well as wetting agents, foam suppressants, flow control agents, stabilizers, catalysts, fillers, plasticizers and solvents.

The polyurethane dispersions according to the invention can also be used directly for gluing any desired substrates. To achieve specific adhesive properties, the polyurethane dispersions according to the invention can be mixed with other dispersions or solutions of plastics (see above). Crosslinking agents, such as, for example, polyisocyanates or prepolymers having terminal isocyanate groups or water-soluble or -emulsifiable melamine or benzoguanamine resins, can furthermore be added to improve the resistance to heat and peeling.

The adhesives based on the polyurethane dispersions according to the invention can contain the additives customary in adhesives technology, such as plasticizers, solvents, film-binding auxiliaries, fillers and synthetic and naturally occurring resins. They are specifically suitable for the production of gluings of substrates in the motor vehicle industry, for example gluing of interior finishings, and in the shoe industry, for example for gluing the shoe sole and shoe shaft. The adhesives based on the polyurethane dispersions according to the invention are prepared and processed by the customary methods of adhesives technology used for aqueous dispersion and solution adhesives.

Example 1:

258.4 g of a polyester prepared from hexane-1,6-diol and isophthalic and adipic acid and having a hydroxyl number of 84 and an acid number of less than 4 are heated to 130°C together with 23.3 g of dimethylolpropionic acid and 0.4 g of hexane-1,6-diol and the mixture is kept at



this temperature until a homogeneous solution exists. 57.3 g of tetramethylxylylene diisocyanate are then metered in over a period of 15 to 20 minutes, while stirring, and stirring is continued at 130°C until free isocyanate groups are no longer present.

After cooling to 70°C, a solution consisting of 80.0 g of methyl methacrylate and 0.1 g of 2,6-di-tert-butyl-4-methylphenol is added rapidly and the mixture is homogenized. 62.9 g of tetramethylxylylene diisocyanate are then added over a period of 15 minutes and the components are reacted at 70°C until the content of free isocyanate groups is 2.12% by weight, based on the total weight. 93.7 g of a reaction product of glycidyl versatate with methacrylic acid are then metered in rapidly over a period of 15 minutes. The reaction is continued at a temperature of 70°C until free isocyanate groups are no longer present. After addition of 12.4 g of triethylamine, the mixture is homogenized for 5 minutes. 1135 g of water having a temperature of 95°C are then added to the prepolymer solution, while stirring intensively. After cooling to 80°C, the mixture is stirred for a further hour. 10% by volume of an ammonium peroxodisulfate solution consisting of 0.8 g of ammonium peroxodisulfate and 50 g of water are added at 80°C to the dispersion thus prepared. The remaining amount of the ammonium peroxodisulfate solution is metered in over a period of 30 minutes.

The temperature is then kept at 78 to 80°C for a further 2 hours.

After cooling to room temperature, the dispersion is filtered through a 5  $\mu$ m filter. The resulting dispersion has a solids content of 32.3% and a pH of 7.50.

Example 2:

282.8 g of a polyester prepared from neopentylglycol, hexane-1,6-diol and isophthalic and adipic acid and having a hydroxyl number of 37 and an acid number of less than 3 are dissolved under reflux in 150 g of acetone together with 28.0 g of dimethylolpropionic acid and 3.3 g of butane-1,4-diol. 112.0 g of 4,4-dicyclohexylmethane diisocyanate are then metered in over a period of 45-60 minutes and the mixture is stirred at the reflux temperature until the content of free isocyanate groups is 1.29% by weight, based on the total weight.

0.1 g of 2,6-di-tert-butyl-4-methylphenol and 67.8 g of a reaction product of glycidyl versatate with methacrylic acid are then added to the prepolymer solution thus obtained. The reaction is continued at the reflux temperature until free isocyanate groups are no longer present. After addition of 18.0 g of triethylamine, 1108 g of water having a temperature of 80°C are added to the polymer solution, while stirring intensively. The acetone solvent is then separated off from the resulting dispersion by vacuum distillation. After addition of 80.0 g of methyl methacrylate, the temperature is increased to 80°C and the mixture is stirred for a further 30 minutes. 10% by volume of an ammonium peroxodisulfate solution consisting of 1.0 g of ammonium peroxodisulfate and 50 g of water is then added at 80°C. The remaining amount of the ammonium peroxodisulfate solution is metered in over a period of 30 minutes. The temperature is kept at 78, to 80°C for a further 2 hours.

After cooling to room temperature, the dispersion is brought to a solids content of 30% and filtered through a 5  $\mu$ m filter. The resulting dispersion has a pH of 7.25.

Example 3:

282.8 g of a polyester prepared from 1,6-hexanediol, isophthalic acid and adipic acid, having a hydroxyl number of 84 and an acid number of 4, are dissolved, together with 28.0 g of dimethylolpropionic acid and 0.7 g of 1,4-butanediol, in 105.0 g of N-methylpyrrolidone at 70°C. 114.5 g of isophorone diisocyanate are then metered in with stirring over a period of from 25 to 30 minutes, and stirring is continued at 70°C until the isocyanate content is 1.40% by weight, based on the total weight of the starting materials.

67.8 g of a reaction product of glycidyl versatate and methacrylic acid, and 0.1 g of 2,6-di-tert.-butyl-4-methylphenol are added rapidly to the prepolymer solution thus obtained, and the mixture is homogenized. The reaction is continued at 70°C until free isocyanate groups are no longer present. After addition of 17.0 g of triethylamine, the mixture is homogenized for 5 minutes. 1022 g of water having a temperature of 95°C are then added to the prepolymer solution while stirring intensively. After cooling to 80°C, 80.0 g of methyl methacrylate are added, and the mixture is stirred for a further 60 minutes. 10% by volume of an ammonium peroxodisulfate solution, comprising 1.0 g of ammonium peroxodisulfate and 50 g of water, are added at 80°C to the dispersion thus obtained. The remaining amount of the ammonium peroxodisulfate solution is metered in over a period of 30 minutes.

The temperature is subsequently kept at 78 to 80°C for a further 2 hours. After cooling to room temperature, the dispersion is filtered through a 5  $\mu$ m filter. The resulting dispersion has a solids content of 33.3% and a pH of 7.35.

The reaction product of glycidyl versatate with methacrylic acid used in Examples 1 to 3 was prepared as

follows:

5 784.5 g of glycidyl versatate are homogenized with  
258.3 g of methacrylic acid, 0.2 g of 2,6-di-tert.-  
butyl-4-methylphenol and 1.04 g of AMC-2 (chromium  
octanoate) at RT. The reactants are then reacted at a  
temperature of 90°C until the acid number is less than 1  
and the epoxide equivalent weight is greater than 10000,  
based on the total weight of starting materials.

Example 4:

10 286 g of a poly(butanediol adipate) (OH number: 45) is  
heated to 130°C together with 23.1 g of dimethylol-  
propionic acid, and the components are reacted with 30 g  
of toluylene diisocyanate at this temperature. After  
cooling to 65-70°C, the mixture is dissolved in 50 g of  
15 stabilized methyl methacrylate, together with 4.7 g of  
hexane-1,6-diol, and reacted with 40.6 g of toluylene  
diisocyanate at 65-70°C. The product is reacted with the  
molar amount of the addition product of glycidyl  
versatate and methacrylic acid which corresponds to the  
20 free NCO content. The mixture is then neutralized with  
12.7 g of triethylamine and dispersed with 683 g of  
deionized water. 50 g of a 2% strength by weight aqueous  
solution of ammonium peroxodisulfate are metered into  
this dispersion at 80°C and the mixture is subsequently  
25 stirred. The resulting dispersion has a solids content  
of 40% by weight, a pH of 7.2 and a dynamic viscosity of  
9 mPas.

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## Patent Claims:

1. A polyurethane dispersion prepared by polymerization, initiated by free radicals, of polyurethane macromonomers containing carboxyl, phosphonic acid or sulfonic acid groups, terminal vinyl groups and optionally urethane, thiourethane or urea groups, the terminal vinyl groups not being derived from hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl (meth)acrylates.
2. A polyurethane dispersion as claimed in claim 1, prepared by polymerization of polyurethane macromonomers which contain carboxyl, phosphonic acid or sulfonic acid groups as well as terminal vinyl groups and optionally urethane, thiourethane or urea groups and are obtained by polyaddition of polyhydroxy-polyethers, polyhydroxy-polyesters or polyhydroxy-polycarbonates, polyhydroxycarboxylic acids, polyhydroxyphosphonic acids or polyhydroxysulfonic acids, and polyisocyanates, and subsequent reaction with a monomer which, in addition to at least one vinyl group, also contains a group which reacts with isocyanate groups, with the exception of hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyl (meth)acrylates, optionally together with primary or secondary amines, alcohols or thioalcohols.
3. A polyurethane dispersion as claimed in claim 1, prepared by polymerization, initiated by free radicals, in a mixture of water and an organic solvent which is inert toward isocyanate groups, if appropriate in the presence of unsaturated monomers which can be copolymerized with the polyurethane macromonomers, and if appropriate removal of the organic solvent by distillation before or after the free radical polymerization.
4. A polyurethane dispersion as claimed in claim 1, wherein the polyhydroxy-polyethers, polyhydroxy-poly-

esters or polyhydroxy-polycarbonates can contain carboxyl, phosphonic acid or sulfonic acid groups.

5        5. A polyurethane dispersion as claimed in claim 1, prepared by polymerization, initiated by free radicals, in an unsaturated monomer which serves as the solvent and is copolymerizable with the polyurethane macromonomers, if appropriate in the presence of further copolymerizable unsaturated monomers.

10       6. The use of a polyurethane dispersion as claimed in claim 1 for the production of coatings on substrates, as an adhesive or as a binder in printing inks.

7. The use of a polyurethane dispersion as claimed in claim 1 for the preparation of metallic and solid base paints in multi-coat build-ups of paint.

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Abstract of the disclosure:

Polyurethane dispersions

Polyurethane dispersions prepared by polymerization, initiated by free radicals, of polyurethane macromonomers containing carboxyl, phosphonic acid or sulfonic acid groups, terminal vinyl groups and optionally urethane, thiourethane or urea groups, the terminal vinyl groups not being derived from hydroxyalkyl (meth)acrylates.

These polyurethane dispersions are suitable for the production of coatings on substrates, as adhesives or as binders in printing inks.



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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for Producing Multi-Layer Lacquer Coatings by  
the Use of Clear Lacquers Which are Capable of  
Polymerisation in Radicalic and/or Cationic Manner

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(30) (DE) P 41 33 290.3 1991/10/08

(57) 13 Claims

Notice: This application is as filed and may therefore contain an  
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Process for producing multi-layer lacquer coatings by the use of clear lacquers which are capable of polymerisation in radicalic and/or cationic manner

The invention relates to a process for producing a multi-layer lacquer coating with a mechanically stable quick-drying clear-lacquer coating based on systems curable by radiation.

Coatings as applied in the series production of automobiles nowadays mostly consist of a surface lacquer of basecoat and clear lacquer which is applied to bodywork that has been electrophoretically primed and coated with filler. In this process basecoat and clear lacquer are preferably applied wet-on-wet, i.e. after a flash-off period optionally subject to heating and after subsequent application of a clear lacquer the basecoat is stoved together with this lacquer, as described for example in EP-A-38 127 and EP-A-402 772. In this connection suitable clear lacquers are described, for example, in EP-A-38 127 and EP-A-184 761. The stoving process in industrial production lacquering requires long drying phases, and naturally a certain time passes before the lacquer is no longer tacky, so that special measures have to be taken in order to avoid incorporating dust in the surface.

Both in the case of the use of one-component (1C) and also of two-component (2C) clear lacquers the lacquering process is associated with emissions of environmentally harmful solvents or dissociation products of the crosslinking reaction. In the case for example of isocyanate-crosslinking 2C clear lacquers, e.g. according to DE-OS 33 22 037 or DE-PS 36 00 425, recycling of overspray is by its nature not possible.

In JP-A-6213 2570 clear UV lacquers are described which serve to protect electrical instruments used in domestic appliances and in the automobile industry. They are applied in a thin film; multiple precoating does not take place.

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In EP-A-0 118 705 and GB-A-2 226 566 UV-curable layers are described for protecting automobile underbodies from the impact of stones. The layers are applied with a thickness of up to 1500  $\mu\text{m}$ . They are formulated so as to be soft and elastic and are not capable of being ground.

In EP-A-0 247 563 coatings are described which by way of surface lacquer have a coating which in addition to an isocyanate-hydroxyl-group crosslinking reaction is also subjected to crosslinking by UV radiation. The overspray accruing during application of the coating agent can in view of the chemical reaction no longer be subjected to recycling.

The object of the invention is to make available a lacquering process for a multi-layer lacquer coating, in particular for the automobile industry, in which a clear lacquer enabling fast crosslinking is used as surface-lacquer coating, in which process the overspray following application can be recycled, and in which a shiny or matt, hard and clear surface lacquer is produced by way of substrate coating.

It has been shown that this aim can be achieved by a process for producing a multi-layer lacquer coating in which a liquid clear lacquer which can be crosslinked exclusively by radicalic and/or cationic polymerisation is applied to a previously dried basecoat layer. Application of the clear lacquer is effected while daylight is screened off, optionally during illumination with visible light having a wavelength of over 550 nm. The overspray accruing during application of the clear lacquer is collected and can optionally be re-used for spraying after recycling. Curing of the clear-lacquer layer is subsequently effected by irradiation with high-energy radiation or is initiated by irradiation with high-energy radiation.

An advantage of the process according to the invention consists in the fact that substrates which are sensitive to

temperature can also be provided with a durable layer of surface lacquer. In addition, as a result of short reaction and drying times, pollution of the freshly lacquered surface can be avoided. The surfaces obtained in this way have good optical characteristics and a high degree of resistance to scratching.

The lacquer systems which can be used according to the invention all make use of coating agents which are curable by radiation and which crosslink exclusively as a result of radicalic or cationic polymerisation or combinations thereof. Aqueous systems rich in solids and occurring as emulsions constitute a preferred embodiment of the invention. But coating agents containing solvents can also be used. Particularly preferred are 100% lacquer systems which can be applied without solvent and without water. The clear lacquers curable by radiation can be formulated as unpigmented or transparently pigmented surface lacquers, optionally coloured with soluble dyestuffs.

The clear-lacquer coatings can be applied to conventional basecoats. These may contain solvents or be of an aqueous or powdery type. The basecoats contain conventional physically drying and/or chemically crosslinking binding agents, inorganic and/or organic colouring pigments and/or pigments producing special effects, such as metallic pigments or those giving a pearly-lustre, as well as other auxiliary substances which are customary in lacquering, such as catalysts, levelling agents or anti-cratering agents. These basecoats are applied to conventional substrates either direct or on pre-coated substrates. Prior to application of the basecoat the substrates can, for example, be provided with conventional primer, filler and intermediate layers such as are customary for, e.g., multi-layer lacquer coatings in the automobile industry. Metal or plastic parts are suitable as substrates.

Prior to coating with radiation-curable lacquers the layers of primer are dried or stoved under such conditions as to ensure that they only contain small amounts of volatile substances. In particular, at the time of the radiation-induced crosslinking reaction of the layer of clear-lacquer coating no substantial amounts of volatile components should any longer be present in the basecoat layer. Such components can impair gloss and adhesion in the clear-lacquer film. Drying of the basecoat layer can be effected at room temperature or at temperatures up to 150°C. This does not exclude the possibility of a chemical crosslinking reaction.

In the particularly preferred case of solvent-free radiation-curable clear-lacquer systems, the process according to the invention enables a particularly good metal effect to be achieved on metallic basecoats by way of basecoat layer.

After application and drying of the basecoat the workpiece is provided with the radiation-curable surface lacquer. Until the workpiece is discharged from the coating unit the coating process is carried out subject to illumination with visible light having a wavelength of over 550 nm or subject to the exclusion of light. To this end necessary measures for screening off other light sources are optionally employed, e.g. light traps at the entrances and exits of the lacquering plant, filters in front of light sources or measures for preventing reflection. Only light sources are used that have an emission spectrum starting at above 550 nm. Such sources are, e.g., lamps provided with UV filters or yellow filters. Illumination can optionally also be effected from outside by the use of windows. During stages of the process which run automatically and need no optical control it is of course possible to proceed subject to the exclusion of light, so that the above-stated light sources only have to be switched on if a fault occurs. In the case of pure electron-ray

curing with suitable lacquer systems work can also proceed under normal lighting conditions.

Application of the radiation-curable lacquer can be carried out by all conventional spray-application methods, such as, e.g., compressed-air spraying, airless spraying, high-speed rotation, electrostatic spray application (ESTA), optionally coupled with hot-spray application such as hot-air spraying, at temperatures not exceeding 70 - 80°C, so that suitable application viscosities are achieved and no change in the lacquer material or the overspray to be recycled occurs during the short time that the thermal treatment is applied. In this way hot spraying can be organised in such a way that the lacquer material is only heated for a short time in the spray jet or a short distance upstream of it.

The spraying booth may optionally be a circulation-type booth of adjustable temperature, operated with an absorption medium suitable for the overspray, e.g. the lacquer material. The spraying booth consists of materials which exclude the possibility of contamination of the material to be recycled and which are not affected by the circulating medium. Examples are high-grade steel or suitable plastics.

By avoiding light with a wavelength below 550 nm the lacquer material used and the overspray are not affected. This enables direct reprocessing. The recycling unit essentially comprises a filtration unit and a mixing device which maintains an adjustable ratio of fresh lacquer material to be reprocessed and optionally circulating lacquer material. In addition, storage containers and pumps as well as control devices are present. With the use of non-100% lacquer material a mixing device is necessary for keeping a constant level of volatile components such as organic solvent components or water.

Application is performed in such a manner that dry layer

thicknesses of preferably 10 - 80  $\mu\text{m}$ , and in particular 30 - 60  $\mu\text{m}$ , are achieved. Application of the clear lacquer can optionally be effected in several layers.

After application of the clear-lacquer coating agent the coated substrate is optionally subjected after a rest period to the crosslinking process. The rest period serves for example to enable levelling, degassing of the lacquer film or evaporation of volatile components such as solvents, water or  $\text{CO}_2$  if the lacquer material has been applied using supercritical carbon dioxide as solvent, as described for example in EP-A-321 607. It can optionally also be supported by increased temperatures of up to  $80^\circ\text{C}$ , and preferably up to  $60^\circ\text{C}$ .

The actual radiation-curing process can be carried out either by UV radiation or electron-ray radiation or with actinic radiation emitted from other radiation sources. In the case of electron-ray radiation it is preferable to work in an atmosphere of inert gas. This can be achieved for example by supplying  $\text{CO}_2$ ,  $\text{N}_2$  or a mixture of both direct to the surface of the substrate.

Use may also be made of an atmosphere of inert gas in the case of UV curing. If a protective gas is not used, ozone may be generated. This can, for example, be extracted by suction.

Preferred radiation sources are UV emitters or electron-ray sources. UV radiation sources having emissions in the wavelength range 180 - 420 nm, and preferably 200 - 400 nm, are, for example:

optionally doped high-pressure, medium-pressure and low-pressure mercury emitters, gas discharge tubes such as low-pressure xenon lamps, pulsed and unpulsed UV lasers, UV spot-type emitters such as UV-emitting diodes. Particularly suitable radiation sources emitting in the longwave UV

spectrum are so-called black-light tubes. Measures can optionally be taken to counter the heat of the radiation source, e.g. by cooling with water or air.

Cathode-ray sources are, e.g., spot-type emitters working according to the electron-ray principle (e.g., made by Polymerphysik, Tübingen) or linear cathodes which work according to the Electrocurtain<sup>R</sup> principle (e.g., made by Energie Science Inc). They have a radiation output of 100 keV to 1 MeV. Combinations of these radiation sources are also possible.

Both the electron sources and the UV radiation sources can also be designed to work discontinuously. Particularly suitable then are laser light sources or electron sources. Another possibility as regards the provision of UV sources capable of being rapidly switched on and off (pulsed operation) consists in the interposing of, e.g., moveable shutters.

By way of auxiliary units use may be made of conventional light-control systems which are customary in the sphere of optics technology, such as absorption filters, reflectors, mirrors, lens systems or light-wave conductors can be employed.

According to the invention irradiation can be carried out in such a way as to ensure that thorough crosslinking of the layer of clear lacquer is effected in one step. It can however also be advantageous to bring about a prior gelling of the coating film by UV-induced crosslinking, e.g. in a first zone in which black-light irradiation takes place, and then to continue crosslinking in a second step or several steps, for example by renewed UV irradiation or by irradiation with electron rays.

The arrangement of the radiation source is in principle

radiation-curable lacquer systems lies in the curing of areas not directly accessible to radiation (shadow zones), e.g. cavities, folds and other undercuts resulting from manufacture. This problem can be solved by, e.g., using spot-type, small-area or omnidirectional emitters with an automatic movement device with a view to irradiating interiors, engine compartments, cavities or edges.

Additionally it is possible to apply a thermal activation in order to bring about crosslinking of the coating agent on surfaces which can only be inadequately subjected to the radiation-crosslinking process. When using coating agents capable of polymerisation in radicalic manner it can be advantageous in this connection to use radical initiators which can be activated thermally, so that subsequent to irradiation or simultaneously with irradiation thermally activated radicalic polymerisation can be achieved. When using cationically polymerisable coating agents it is not necessary to use special initiators which can be activated thermally. The cationic polymerisation initiated by the radiation energy also spreads to the shadow zones, e.g. the unirradiated or only slightly irradiated surfaces. It is however also advantageous in this case to apply heat in order to support polymerisation in the shadow zones.

According to the invention radiation-curable clear-lacquer coating agents can be used which are well-known in principle and described in the literature. This involves either systems which are curable in radicalic manner, i.e. by the effect of radiation on the coating agent radicals are formed which then trigger the crosslinking reaction, or systems which are curable in cationic manner, in which by irradiation of initiators Lewis acids are formed and serve to trigger the crosslinking reaction.

Systems which are curable in radicalic manner make use of, e.g., prepolymers, such as polymers or oligomers which have



well-known and can be adjusted to suit the conditions of the workpiece and the parameters of the process.

For example, the workpiece can be irradiated as a whole, or a radiation curtain can be used which moves in relation to the workpiece. In addition, by the use of an automatic device a spot-type radiation source can be passed over the substrate and initiate the crosslinking process. In order to achieve a crosslinking reaction on all sides of the workpiece, movement of the substrate in front of the radiation sources about the longitudinal or transverse axes is also possible.

The distance of the radiation source can be fixed or it can be adapted to a desired value according to the form of the substrate. The distances of the radiation sources from the wet-lacquer surface preferably lie in the range from 2 to 25 cm, and in particular 5 - 10 cm. If a UV laser is used, a greater distance is possible.

Of course, the process steps listed as examples can also be combined. This can be effected in a single stage of the process or in process stages temporally or spatially separated from one another.

The duration of irradiation lies for example in the range from 0.1 seconds to 30 minutes, according to lacquer system and radiation source. A duration of less than 5 minutes is preferred. The duration of irradiation is chosen in such a way as to achieve total curing, i.e. the formation of the required technological characteristics is ensured.

The process according to the invention can be used to particular advantage in the production of multi-layer lacquer coatings in the automobile industry, e.g. in the manufacture of car bodies or their parts.

A problem with the coating of automobile bodies with

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olefinic double bonds in the molecule. These prepolymers can optionally be dissolved in reactive diluents, i.e. reactive liquid monomers. In addition, coating agents of this type can also contain conventional initiators, light-ray-absorbing agents and, optionally, transparent pigments, soluble dyestuffs and additional auxiliary lacquering agents.

Examples of prepolymers or oligomers are (meth)acrylic-functional (meth)acrylic copolymers, epoxide resin (meth)acrylates which are free of aromatic structural units, polyester(meth)acrylates, polyether(meth)acrylates, polyurethane(meth)acrylates, unsaturated polyesters, amino(meth)acrylates, melamine(meth)acrylates, unsaturated polyurethanes or silicon(meth)acrylates. The molecular weight (number average  $M_n$ ) lies preferably in the range from 200 to 10000, and in particular from 500 to 2000. Here and in the following (meth)acrylic denotes acrylic and/or methacrylic.

If reactive diluents are employed they are generally used in quantities between 1 and 50% by weight, preferably 5 - 30% by weight, relative to the total weight of prepolymers and reactive diluents. They can be mono-, di- or polyunsaturated. Examples of such reactive diluents are: (meth)acrylic acid and its esters, maleic acid and its semi-esters, vinyl acetate, vinyl ether, substituted vinyl carbamides, alkylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)acrylate, glycerine tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, styrene, vinyl toluene, divinyl benzene, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate and hexanediol di(meth)acrylate, as well as mixtures thereof. They serve to influence viscosity and technical lacquering characteristics, such as, e.g., the crosslinking density.

Photoinitiators for systems curable in radicalic manner can, e.g., be used in amounts from 0.1 to 5% by weight, preferably 0.5 - 3% by weight, relative to the total quantity of prepolymers which are polymerisable in radicalic manner, reactive diluents and initiators. It is advantageous if their absorption range is within 260 - 450 nm. Examples of photoinitiators are benzoin and derivatives, benzil and derivatives, benzophenone and derivatives, acetophenone and derivatives, e.g., 2,2-diethoxyacetophenone, thioxanthone and derivatives, anthraquinone, 1-benzoylcyclohexanol, organophosphorus compounds such as acylphosphine oxide. The photoinitiators can be used on their own or in combination. In addition, other synergistic components, e.g. tertiary amines, can be used.

In addition to the photoinitiators, conventional photosensitisers such as anthracene can also be used, if necessary, in the usual quantities, for example with a view to irradiation with black-light tubes. Additionally, radicalic initiators which can be activated thermally can optionally be used. Between 80 and 120°C these form radicals which then start the crosslinking reaction. Examples of thermolabile radicalic initiators are: organic peroxides, organic azo compounds or C-C-dissociating initiators such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azodinitriles or benzpinacolsilyl ethers. C-C-dissociating initiators are particularly preferred, since with thermal dissociation no gaseous reaction products are formed which can cause faults in the lacquer coating. The preferred quantities to be used are between 0,1 and 5% by weight relative to the total quantity of prepolymers which are polymerisable in radicalic manner, reactive diluents and initiators. The initiators can also be used in a mixture.

Binding agents for cationically polymerisable coating agents are for example polyfunctional epoxy oligomers which contain

more than two epoxy groups in the molecule. It is advantageous if the binding agents are free from aromatic structures. Such epoxy oligomers are, for example, described in DE-OS 36 15 790. They are, for example, polyalkylene glycol diglycidyl ethers, hydrated bisphenol-A glycidyl ethers, epoxy urethane resins, glycerine triglycidyl ethers, diglycidylhexahydrophthalate, diglycidyl esters of dimeric acids, epoxidated derivatives of (methyl)cyclohexene such as 3,4-epoxycyclohexyl-methyl-(3,4-epoxycyclohexane)carboxylate or epoxidated polybutadiene. The number average molecular weight of the polyepoxide compounds preferably lies below 10000.

If low viscosities are needed for application they can be adjusted by the use of reactive diluents, i.e. reactive liquid compounds such as cyclohexene oxide, butene oxide, butanediol diglycidyl ether or hexanediol diglycidyl ether. Examples of additional reactive solvents are alcohols, polyalkylene glycols, polyalcohols, hydroxy-functional polymers, cyclic carbonates or water. These can also contain solid constituents in solution, for example solid polyalcohols such as trimethylolpropane.

Photoinitiators for cationically curable systems are used in amounts from 0.5 to 5% by weight, on their own or in combination, relative to the total quantity of cationically polymerisable prepolymers, reactive diluents and initiators. There are substances known as onium salts which when irradiated give rise photolytically to Lewis acids. Examples are diazonium salts, sulfonium salts or iodine onium salts. Particularly preferred are triarylsulfonium salts.

Non-reactive solvents for systems which are curable in radicalic and cationic manner are conventional lacquer solvents such as esters, ethers, ketones, for example butyl acetate, ethylene glycol ether, methylethyl ketone, methylisobutylketone, as well as aromatic hydrocarbons. For

systems which are polymerisable in radicalic manner  $C_2-C_4$ -alkanols, and preferably water, are also suitable as solvents.

The clear lacquers used according to the invention preferably have light-ray-absorbing agents added to them. Examples of these are phenyl salicilates, benzotriazole and derivatives, HALS compounds, as well as oxalanilide derivatives, optionally also used in combination. Customary concentrations amount to 0.5 to 5% by weight, preferably 1 - 2% by weight, relative to the total quantity of clear lacquer. When choosing the light-ray-absorbing agent, attention must be given to ensuring that the initiation of crosslinking is not impaired by the light-ray-absorbing agent and that such agents that are used are stable when irradiated during the radiation-curing process.

Further additives are, for example, elastifying agents, polymerisation inhibitors, defoamers, levelling agents, anti-oxidation agents, transparent dyestuffs or optical brightening agents.

Transparent colourless fillers and/or pigments can optionally be added to the coating agent. The amount used is up to 10% by weight, relative to the total amount of clear lacquer. Examples are silicon dioxide, mica, magnesium oxide, titanium dioxide or barium sulphate. The size of the particles preferably lies below 200 nm. With UV-curable systems attention should be given to ensuring that the coating film in the layer thickness used remains transparent to UV radiation. Additional useable additives are, for example, conventional inorganic or organic delustering agents. These can be added in conventional amounts, for example up to 10% by weight. Examples of delustering agents are silicates, pyrogenic silicic acids such as aerosil, bentone or condensed and crosslinked urea formaldehyde resins, natural and synthetic waxes. The particle sizes of such delustering

agents lie generally in a range up to 100  $\mu\text{m}$ , and preferably up to 30  $\mu\text{m}$ .

The stages of the process for producing suitable radiation-curable clear-lacquer coating agents are well-known. It is possible to combine systems with different radiation-induced chemical crosslinking mechanisms. These can be various crosslinking systems curable in radicalic manner, or cationically curable crosslinking systems, or radically and cationically curable crosslinking combined with one another. Attention should be given to choosing the composition in such a way as to ensure long storage life. Likewise different reaction-initiating processes can be combined, for example UV with UV curing, UV with thermal initiation or electron-ray curing with UV curing.

The various crosslinking reactions can be started with mixtures of suitable initiators. For example, mixtures of UV initiators with differing maximum absorption characteristics are possible. In this way various emission maxima of one or several radiation sources can be utilised. This can be effected simultaneously or in sequence. For example, curing can be initiated with radiation from one radiation source and continued with that from another. The reaction can then be carried out in two or more stages, optionally also separated spatially. The radiation sources used can be the same or different.

According to the invention it is possible to carry out firstly a radiation-induced and then or simultaneously a thermally induced crosslinking reaction. To this end, in addition to one or several photoinitiators, one or several thermally dissociating initiators can optionally be used. The use of photoinitiators is not necessary when curing by electron rays.

Two- or multi-stage operation can be advantageous, in order,

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for example, to achieve initial gelling, whereby for example runs on lacquered vertical surfaces can be avoided. Gelling is also advantageous in the case of solvent-based systems, in order to allow evaporation of the solvent.

The photoinitiators are preferably chosen in such a way that they do not decay in light having a wavelength of over 550 nm. With the use of thermally dissociating initiators these should be chosen in such a way as to ensure that they do not decay under the conditions of application of the lacquer material. In this way it is possible to recycle the overspray of the coating agent directly and to re-use it, since a chemical reaction is avoided during application.

The crosslinking density of the lacquer films can be adjusted by the functionality of the components of the binding agent employed. The choice can be made in such a way as to ensure that the crosslinked clear-lacquer coating has sufficient hardness and that too high a degree of crosslinking is avoided, in order to prevent the film from becoming too brittle.

By means of the process according to the invention multi-layer coatings are obtained which constitute a clear-lacquer surface with high resistance to scratching and also a high degree of gloss, as well as a high degree of mechanical durability. As a result of the process parameters and the chosen crosslinking mechanism, at the same time the overspray of the coating agent to be applied can be made available for immediate re-use. The process according to the invention is particularly suitable for use in series production lacquering in the automobile industry; for example, for the lacquering of car bodies and their parts.

In all the examples described below, application of the radiation-curable clear lacquers was performed in a room illuminated exclusively by red-light sources (light

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wavelength greater than 600 nm).

Example 1

By mixing the following components a radiation-curable clear-lacquer coating agent was formed:

% by weight

44.5	Novacure 3200	(aliphatic epoxy acrylate made by Interorgane)
32.2	Ebecryl 264	(aliphatic urethane acrylate made by UCB)
3.0	Irgacure 184	(photoinitiator made by CIBA)
10.0	dipropylene glycol diacrylate	
10.0	trimethylolpropane triacrylate	
0.3	Ebecryl 350	(silicon acrylate made by UCB)

Subsequently a lacquer structure was produced as follows:

A metal plate with a primer composed of KTL (20  $\mu$ m) and pre-coated with filler which is customary in the trade (35  $\mu$ m) was coated in one case with conventional water-based lacquer, in a second case with solvent-containing basecoat (15  $\mu$ m dry layer thickness), and then in both cases stoved for 20 min at 140°C. Subsequently the above lacquer system was applied with a layer thickness of 35  $\mu$ m.

Given a belt velocity of 9 m/min, curing of the horizontal metal test plate was effected by irradiation by two medium-pressure mercury emitters, each of which having an output of 100 W/cm and placed at a distance of 10 cm from the surface to be cured (duration of irradiation 1 - 2 sec). A shiny and hard surface with good adhesion was obtained on both the aqueous basecoat and the conventional basecoat.



Example 2

% by weight

40.5 Novacure 3200

27.5 Ebecryl 264

2.0 C-C-dissociating initiator (tetraphenylethane  
derivative according to  
DE-A-1 219 224)

2.0 Irgacure 184

10.0 dipropylene glycol diacrylate

10.0 tripropylene glycol diacrylate

0.3 Ebecryl 350

7.7 vinyl toluene

A metal test plate was produced in a similar way to that described in Example 1, in this case however coated on both sides, and after application of the above radiation-curable clear lacquer it was irradiated on just one side while freely suspended, the side to be irradiated being moved evenly, at a distance of 10 cm and within 5 sec, past a medium-pressure mercury emitter as stated in Example 1.

The tacky rear side which was only partially crosslinked by irradiation was stoved for 15 min at 110°C in an air-circulating furnace.

Surfaces were obtained on both sides of the metal test plate with characteristics as described in Example 1.

Example 3

(radiation-induced cationically curable clear lacquer)

% by weight

60.0 Degacure K 126 (cycloaliphatic epoxide made by  
DEGUSSA)

25.0 Araldit DY 026 (hexanediol diglycidyl ether made by  
CIBA)

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- 4.5 Degacure KI 85 (sulfonium salt made by DEGUSSA)
- 0.5 Dynasilan Glymo (glycidyl-functional silane made by  
Dynamit Nobel)
- 10.0 cyclohexanol

With this formulation the procedure was completely analogous to that in Example 1. A similar lacquer was obtained.

#### Example 4

Example 1 was repeated, with the same lacquer result. The only difference being that the basecoat layers here were stoved for 30 min at 120°C and pre-coated polycarbonate sheets were used.

#### Example 5

To 100 parts of the clear-lacquer coating agent from Example 1, two parts of anthracene were added as photosensitiser. Application was effected as described in Example 1. Then irradiation was effected at a belt velocity of 1 m/min, lying flat, with 10 black-light tubes at a distance of 10 cm from the wet-lacquer surface (duration of irradiation 90 - 120 sec). A tacky, partially crosslinked surface was obtained. Then the metal test plate was suspended for 5 min and then, hanging free, irradiated, the still tacky surface being moved uniformly, at a distance of 10 cm and within 5 sec, past a medium-pressure mercury emitter as stated in Example 1. A lacquer result as stated in Example 1 was obtained. The surface was free from runs.

CLAIMS

1. Process for producing a multi-layer lacquer coating by the application of a clear lacquer coating to a dried or crosslinked basecoat film which is coloured and/or has a special finish, characterised in that in order to produce the clear-lacquer coating a coating agent is used which is curable exclusively by radicalic and/or cationic polymerisation, application of the coating agent being effected subject to illumination with light having a wavelength of over 550 nm or subject to the exclusion of light, whereupon curing is initiated and/or implemented by high-energy radiation.
2. Process according to Claim 1, characterised in that curing is initiated and/or implemented with UV radiation in the wavelength range from 180 to 420 nm.
3. Process according to any of the preceding Claims, characterised in that curing is initiated and/or implemented by irradiation with electron rays.
4. Process according to any of the preceding Claims, characterised in that curing is effected by two or several high-energy sources of radiation in succession in two or more stages.
5. Process according to any of the preceding Claims, characterised in that after initial curing by high-energy radiation curing is additionally effected by thermal means or is continued by thermal means.

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6. Process according to Claim 5, characterised in that it is carried out with a coating agent curable by radicalic polymerisation and which contains one or several photoinitiators and one or several radical initiators which are capable of being activated thermally.
  7. Process according to Claim 5, characterised in that it is carried out with a coating agent curable by cationic polymerisation and which contains one or several photoinitiators.
  8. Process according to any of the preceding Claims, characterised in that it is carried out with a coating agent containing transparent pigments and/or soluble dyestuffs.
  9. Process according to any of the preceding Claims, characterised in that a coating agent is used which is essentially free from solvents or contains water as solvent.
  10. Process according to any of the preceding Claims, characterised in that the clear lacquer coating is applied with a dry layer thickness of 10 - 80  $\mu\text{m}$ .
  11. Process according to any of the preceding Claims, characterised in that the coating agent is applied by spray and overspray accruing is optionally recycled for spray application after replacement of volatile components.
  12. Use of transparent coating agents as clear lacquers in producing multi-layer lacquer coatings which are curable by radicalic and/or cationic polymerisation and optionally contain transparent pigments and/or soluble dyestuffs.

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13. Use according to Claim 12 in the production of multi-layer lacquer coatings in the automobile industry.

Herberts GmbH

Process for producing multi-layer lacquer coatings by the use of clear lacquers capable of being polymerised in radicalic and/or cationic manner

ABSTRACT

Process for producing a multi-layer lacquer coating by the application of a coat of clear lacquer consisting of coating agents which are curable exclusively by polymerisation in radicalic and/or cationic manner to a dried or crosslinked coloured and/or effect-producing basecoat film, the process taking place in light having a wavelength of over 550 nm or subject to the exclusion of light, this being followed by initiation or implementation of curing of the clear-lacquer film by high-energy radiation. The process is particularly suitable for producing multi-layer lacquer coatings in the automobile industry.